

PLASTIC DEFORMATION OF POLYCRYSTALLINE NICKEL THERMALLY CHARGED WITH HYDROGEN

By
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DEPARTMENT OF METALLURGICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
AUGUST 1976

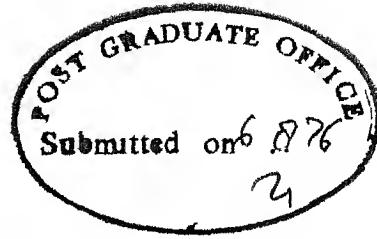
PLASTIC DEFORMATION OF POLYCRYSTALLINE
NICKEL THERMALLY CHARGED
WITH HYDROGEN

A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY

By
VINAY KUMAR GARG

to the

DEPARTMENT OF METALLURGICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
AUGUST, 1976



(i)

CERTIFICATE

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out under my supervision and it has not been
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M N Shetty

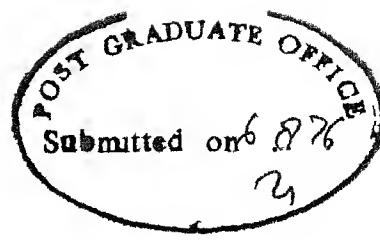
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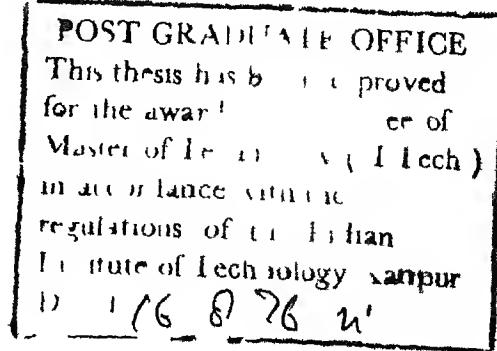
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NOMENCLATURE

A	=	Proton energy in an unstrained area
α	=	Dimensionless quantity signifying number of electrons within a sphere of radius r
b	=	Burger vector
C	=	Concentration of dissolved hydrogen
C_3, C_4	=	Material constants
D	=	Diffusion coefficient of solute
Δ	=	Dialatation = $\frac{b}{2\pi} \frac{1-2\nu}{1-\nu} \frac{\sin\theta}{R}$
e	=	electronic charge
ϵ	=	Strain rate
ϵ_c	=	Critical strain rate
$\phi(r)$	=	Electrostatic potential at radius r
G	=	Shear modulus
μ	=	Dirac constant
I	=	Atmosphere radius
k	=	Boltzmann constant
k_{\max}	=	Wave number of highest occupied state
K, K', K''	=	Equilibrium constants
m	=	Electronic mass
n	=	Material constant
N	=	Total number of electrons per unit volume
ν	=	Poisson ratio
P	=	Pressure of hydrogen
P_H	=	Partial pressure of atomic hydrogen in metal
P_{H_2}	=	Partial pressure of molecular hydrogen in metal

ρ	=	Dislocation density	(2 5)
ρ	=	Charge density	(4 9)
Q	=	Heat of solution	
$q(r)$	=	Charge around a proton within a sphere of radius $r < r_s$	
R	=	Gas constant	
r, r_s	=	Radius of sphere	
s	=	Solubility of hydrogen	
s_0	=	Constant	
σ	=	Stress	
σ_0	=	Yield stress at $T = 0^\circ K$	
σ_y	=	Yield stress at a given temperature $T^\circ K$	
$\sigma_{y\epsilon_1}$	=	Yield stress at strain rate ϵ_1	
$\sigma_{y\epsilon_2}$	=	Yield stress at strain rate ϵ_2	
$\Delta\sigma$	=	Difference in yield stress at ϵ_2 and ϵ_1	
T	=	Temperature, $^\circ K$	
U	=	Activation energy	
U_c	=	Electrostatic energy of interaction of a proton with electrons	
U_F	=	Average kinetic energy of Fermi gas	
U_d	=	Proton - dislocation interaction energy	
$U_o(r_s)$	=	Total energy per atom	

ABSTRACT

Hydrogen charged nickel is known to exhibit serrated yielding over a range of temperatures when tested in tension below room temperature. This is examined in detail by measuring activation energy from strain rate change experiments performed at different temperatures and by using analysis similar to those available for dilute Fe-C alloys. The activation energy estimated is in general agreement with those energies available in literature, but is found to be strongly temperature dependent. Consistent with the available suggestions, this is interpreted by considering the hydrogen interaction with edge dislocations as a proton and an electron with the electrons getting into unfilled bands of nickel. A method of calculating variable binding energy for such a configuration is also given.

CHAPTER 1

INTRODUCTION

The correlation of strain rate sensitivity, temperature and hydrogen concentration with the degree of hydrogen embrittlement has been extensively studied for both ferrous as well as non-ferrous metals and alloys [1]. The loss of ductility and embrittlement becomes more severe by slow strain rates and moderate temperatures and it has been suggested that diffusion of hydrogen atom is one of the possible rate controlling mechanisms [2]. Among the face centered cubic metals, serrated yielding in hydrogen charged polycrystalline nickel has been studied in several investigations over a range of temperatures [3-9]. In nickel serrated yielding is found to start at an Upper Critical Temperature (UCT) and disappear at a Lower Critical Temperature (LCT). Some of these authors have considered hydrogen atom - dislocation interaction, as suggested by Bastien and Azou [10], and estimated activation energy for interaction at UCT and LCT. Blakemore [6] considered specific mechanisms like elastic interaction between hydrogen atom and a dislocation, Suzuki locking and local order interaction.

The spread in activation energies estimated by several investigators were generally attributed to experimental errors, purity of nickel and difference in hydrogen concentration. In the present investigation, activation energies are determined by using analysis available for dilute Fe-C alloys and assuming that the dislocation release process in the two systems are similar.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The damaging effect of hydrogen in many alloy systems, including steels [11-15], titanium and titatium alloys [12,16,17] and nickel and nickel base alloys [3-9,12,18] has been well established in the past two decades. The first observation of the effect of hydrogen on the physical properties of iron was reported, a century ago, by W. J. Johnson from Manchester, who found extraordinary decrease in toughness and fracture stress of the iron caused by its temporary immersion in hydrochloric acid and sulphuric acid. Pfiel, in 1926, found that the presence of hydrogen in steel caused a considerable loss of ductility at room temperature under normal tensile conditions.

Hydrogen embrittlement can result from hydrogen dissolved in the liquid metal, from hydrogen adsorption during electrodeposition operations, and from hydrogen pickup where the metal is exposed to hydrogen in the gaseous form or to hydrogen resulting from the reaction of high temperature water or steam with the metal.

Generally, the amount of hydrogen required to produce embrittlement depends upon the metal or alloy system under consideration, the degree of prior deformation, the strain rate imposed on the metal and the temperature

It should not be inferred that the presence of hydrogen in metals is always deleterious. When present in amounts less than that necessary for embrittlement, hydrogen can cause a noticeable increase in strength so long as it can be retained in solution.

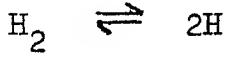
2 2 HYDROGEN-METAL RELATIONSHIPS

2 2 1 General Smithells [19] recognizes that three main processes can occur when a gas is in contact with metal. Firstly, the gas may condense on to the metal surface forming a layer, the thickness of which is of the order of one or two molecules, this is known as adsorption. Secondly, the gas may enter into solution within the interior of the metal, this process is referred to as absorption, or as occlusion. Thirdly the occluded gas may then diffuse through the interior of the metal. The term sorption is used to refer to duplex condition when the gas may be present in both the adsorbed and absorbed states.

Smithells explanation of the solubility of gases in metals depends upon statistical mechanics. He regards the metal as containing a series of "holes" of low potential energy, distributed throughout the lattice. The precise distribution of these holes depends upon the particular lattice structure of the metal.

Siever's Law, governing solubility of a gas as a function of temperature, for hydrogen in a metal can be derived as follows

At any temperature, equilibrium is reached when the rate of formation of nascent and molecular hydrogen is equal



mass action constant can be given by

$$K = \frac{(PH)^2}{(PH_2)}$$

Hence $PH = K(PH_2)^{1/2}$

$$PH_2 = K(PH)^2 \quad (21)$$

Using Henry's Law, which states that the concentration of hydrogen in a metal at a given temperature is proportional to the partial pressure

of the hydrogen in it, or

$$C = K' PH \quad (22)$$

Thus, from equations (21) and (22) above, it follows that the amount of hydrogen dissolved at a given temperature is proportional to the square root of the gas pressure outside the metal, or

$$C = K'' (PH_2)^{1/2} \quad \text{Sievert's Law} \quad (23)$$

Sievert's law requires the gas to be present in atomic form and excludes the possibility of molecular diffusion suggested by Smithells

2.2.2 Hydride Formation The term "hydride" is defined, in generic sense, as the binary combination of hydrogen and a metal or metalloid. Gibbs has defined a hydride as a compound in which there is a metal-to-hydrogen bond.

The classification of hydrides is done on the basis of hydrogen bond. There are four possible types of interaction which can occur when a metal is in contact with hydrogen, thus [13]

(a) Strongly electropositive alkali metals and alkaline earth metals react with hydrogen to form salt-like or saline hydrides. Saline hydrides are highly polar

because of strong electrostatic forces existing between the dissimilar electric charges of the two ions. These salt like hydrides are crystalline, exhibit high heats of formation and high melting points, and are electrical conductors in the molten state.

(b) The metals of groups IV B, VB and VIB form covalent hydrides. The bond between hydrogen and the element is of the nonpolar electronsharing type where valence electrons are shared on a fairly equal basis between the elements held by the bond. In general, molecules of covalent hydrides are not strongly attached to each other, and this absence of strong intermolecular forces results in the high degree of volatility and low melting points of the covalent hydrides. The covalent hydrides are generally thermally unstable, such instability increasing with increasing atomic weight of the parent element.

(c) Many metals form true solid solutions with hydrogen in accordance with Sievert's law. Here the hydrogen take up increases as the temperature increases (Fig. 21). These metals are known as endothermic occluders. These metals include those of greatest practical importance, particularly the metals of the iron group, chromium, copper, nickel and platinum.

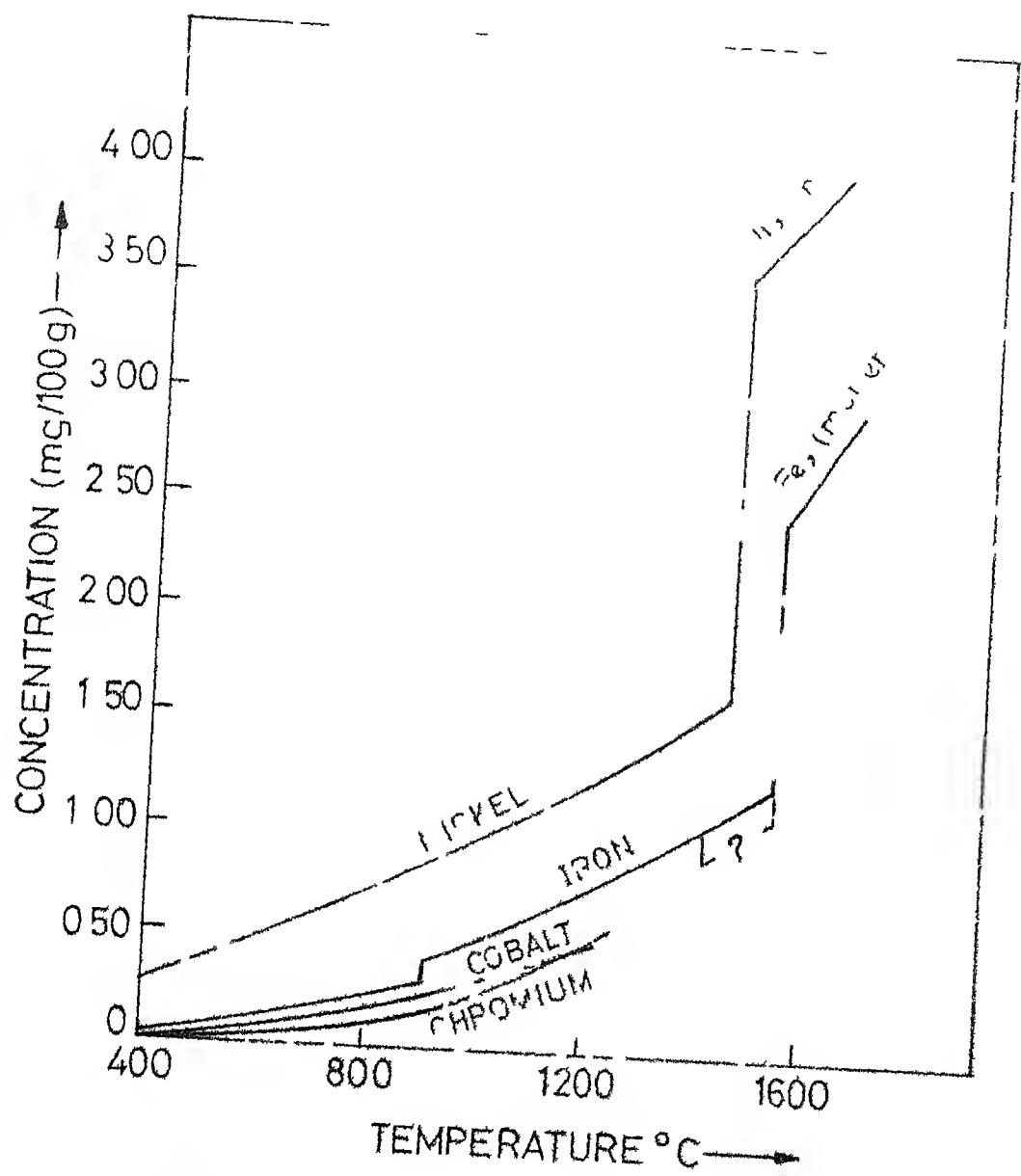


FIG 21 SOLUBILITY ISOBARS OF ENDOTHERMIC OCCLUDERS AT 1 ATMOSPHERE

Considering Sieverts' law and temperature dependence of concentration of hydrogen in metal leads to following expression for endothermic occluders

$$S = S_0 \sqrt{P} \exp(-Q/2RT) \quad (24)$$

(d) Hydrogen forms 'pseudo-hydrides' with metals of group IVA and VA together with the rare earths and the 'actinides'. Since, the amount of hydrogen decreases with increasing temperature, these are known as exothermic occluder (Fig 22). These occluders have maximum capacity to absorb hydrogen

The only reaction with hydrogen is the formation of a simple solid solution, the extent of which varies according to the pressure of the gas and the temperature. However, the behaviour is complicated by the formation of pseudo-metallic hydrides. Here it is important to distinguish between the solubility of hydrogen and the total amount of hydrogen which is absorbed by the metal

2.3 Effect of Hydrogen on Mechanical Properties

The correlation of strain rate sensitivity, temperature, and hydrogen concentration with the degree of hydrogen embrittlement has been extensively studied for both ferrous as well as non-ferrous metals and

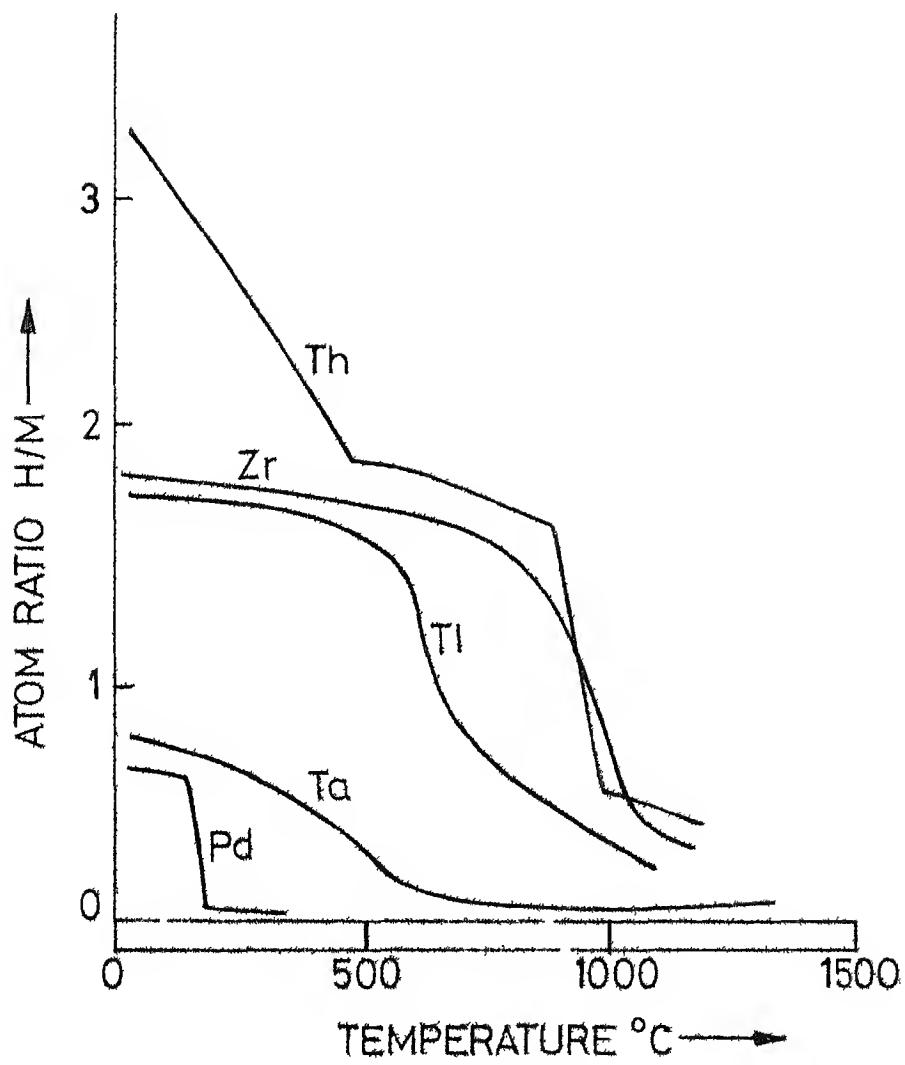


FIG 2 2 SOLUBILITY ISOBARS OF EXOTHERMIC OCCLUDERS AT 1 ATMOSPHERE

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alloys [20] The loss of ductility and embrittlement becomes more severe by slow strain rates and moderately elevated temperature [2] This slow strain-rate and temperature sensitivity indicates that the phenomenon of hydrogen embrittlement is controlled by the lattice diffusion of hydrogen

Above discussion does not imply that hydrogen deteriorate all mechanical properties Hydrogen does not change the shape of stress-strain curve, it reduces yield stress by a little amount and fracture occurs at lower strain levels There is no influence on impact strength, elastic properties and hardness but the endurance limit and fatigue life is impaired by the introduction of hydrogen

The most important factor is that there is a lower critical stress, below which delayed failure will not occur [3,4] This can be readily explained by considering Cottrell's formula [21] for the critical strain rate, ϵ_c , above which a dislocation break away from its atmosphere.

$$\epsilon_c = \frac{4D\beta b}{I} \quad (2.5)$$

Since $\frac{4b}{I} \approx 1$, the equation (2.5) modifies in to

$$\epsilon_c = D\beta \quad (2.6)$$

But there is upper limit of strain rate above which

embrittlement will not occur. Because at higher ϵ_c dislocation density increases. This explains why there is no embrittlement effect on impact test because strain rate is too fast to permit embrittlement to take place.

2.4 Theories of Hydrogen Embrittlement

It would seem appropriate at this time to discuss some of the existing theories of hydrogen embrittlement. The first theory, known as Planer Theory was given by Zapffe [22]. He considered the precipitation of molecular hydrogen in voids with a build up of high localised pressure which produces a high degree of localized triaxial stresses thereby inhibiting extensive slip and restriction of plastic deformation resulting in the brittle failure.

Bastein and Azou [10] modified the above planer theory by considering hydrogen concentration around dislocation as a Cottrell atmosphere. Under the influence of stresses these atmosphere travel through the lattice. Whenever it reaches a void, some of the hydrogen is discharged into it causing embrittlement.

Kazinczy [23] considers the expansion of the gas during the crack growth as being responsible for the energy necessary for crack propagation because of

the fact that expansion of a gas is accompanied by the release of the energy. This release of energy lowers the applied stress necessary for crack propagation. Continued crack growth depends upon continued increase in energy content of the gas in the crack which is being provided by hydrogen diffusion to the crack and precipitation therein.

Petch [24] attributed fracture to the formation of a crack ahead of an array of dislocations piled up against a grain boundary. The stress required for fracture is lowered as a result of adsorption of hydrogen on the surface of the crack as it forms. The embrittlement is found to disappear at high strain rates and low temperatures.

Vaughan and De Morton [25] has considered the idea of a strain hardening effect, based on an original suggestion made by Azou and Bastien [10], as a result of Cottrell - type atmosphere which interfere with the movement of dislocation in the metal lattice. The emphasis is given on the fact that the hydrogen atmospheres are said to be formed on straining and they are not present in unstrained metal. Hydrogen is thought to be initially present in interstitial solution, but on the application of stress, it diffuses to the active slip

planes forming atmospheres which hinder the movement of dislocations and lead to premature fracture

Morlet and coworkers [26] have suggested hydrogen embrittlement mechanism considering the presence of hydrogen in the voids and the distribution of the hydrogen in solution with the lattice of the metal. The effect is considered to be because of combined effect of hydrogen and stress. He considered voids as being internal notches which act as points of stress concentration. On the application of stress, a multi-axial stress system is established around each void. He emphasised that the severity of embrittlement depends not on the hydrogen within the voids but rather on the hydrogen concentration within those regions at which the tri-axiality of the stress system is maximum.

Troiano [14] suggested that crack propagation is a discontinuous process and consists of a series of crack initiations. The most severe triaxial-stress state will arise just slightly in advance of the crack. When the critical hydrogen concentration is attained, a small crack forms and grows through the hydrogen-enriched region, thus joining the previous crack. Further crack growth must await diffusion of hydrogen to the new region of high stress state.

Westlake [27] has proposed a generalized model of hydrogen embrittlement of metals. The proposed model is based on the premise that the hydrogen embrittlement of any metal can be explained in terms of localized formation of a phase whose mechanical properties differ from those of the matrix because of the hydrogen enrichment.

2 5 Nickel - Hydrogen System

Nickel falls under the category of endothermic occluders. Fig 21 shows the variation of concentration of hydrogen as a function of temperature. Nickel saturated with hydrogen from a gaseous atmosphere or from cathodic charging or deposition has been studied by X-ray [12]. The conclusion reached was that hydrogen has virtually no effect on the lattice parameter of nickel. But Boniszewski and Smith [28] have given evidence for the existence of a face centered cubic nickel hydride by indexing the diffraction patterns. They showed that the hydride structure is expanded about 5½% over the metal structure, the lattice parameter of hydride being 3.721 Å. They have reported the ratio of hydrogen atoms to nickel atom of approximately 0.8 from the determination of the hydrogen concentration in the surface layer transformed to hydride resulting

in NiH type formula for nickel hydride. A neutron diffraction study [29] of nickel hydride established that the hydrogen atoms occupy octahedral interstices of the face centered cubic metal lattice. The occupation of octahedral sites establish the fact that NiH type of structure is most probable because coordination number of both nickel and octahedral interstices is 4.

Nickel hydride is very unstable and decomposes within ~ 40 hr at room temperature. The enthalpy of dissociation of the hydride in the range $H/Ni = 0.3$ to 0.5 is 2.4 ± 0.1 Kcal per mole of hydrogen at $25^\circ C$ [30].

There are three methods of charging nickel with hydrogen. First method [31] involves charging specimen at atmospheric or slightly higher pressure at elevated temperature, allowing the specimen to equilibrate with it, and then quenching the specimen in ice bath to retain hydrogen in supersaturation.

The second method involves hydrogen charging at very high pressures at room temperature which can be accomplished directly with a gaseous hydrogen atmosphere or indirectly by using cathodic charging in a suitable electrolyte [3]. Cathodically charging can completely transform the surface layer to hydride with

the depth of the layer increasing with charging time. Keeping specimens at room temperature, after charging, involves decomposition of the unstable hydride resulting in hydrogen evolution preferentially from the grain boundaries, and thus cracks are generated in grain boundaries with occasional transgranular cracks.

The third method involves thermal charging, also known as hydrogen annealing [4]. In this case hydrogen charging is obtained by heating specimens in a dry H_2 atmosphere at temperatures of the order of $900^\circ C$, allowing the specimens to equilibrate for about one hour and then quenching in ice water and keeping samples in liquid N_2 until tensile testing.

2 6 Serrated yielding in Hydrogen charged Nickel Poly - Crystals

The effect of hydrogen in nickel has been extensively investigated by several investigators [3-9]. The pioneering work was done by Boniszewski and Smith [3] who performed tensile tests on cathodically charged nickel samples at various temperatures ranging from room temperature to liquid nitrogen temperature. The strain rates used were from 3.33×10^{-4} to $8.33 \times 10^{-1} \text{ Sec}^{-1}$. He found that serrated yielding started around $-50^\circ C$ and

it was termed as Upper Critical Temperature and it disappeared at about -110°C and this temperature was termed as Lower Critical Temperature Wilcox and Smith [4] also observed serrated yielding in hydrogen charged polycrystalline nickel (61 cc $\text{H}_2/100$ g Ni) at -80°C at different strain rates from 1.1×10^{-6} to $1.1 \times 10^{-2} \text{ Sec}^{-1}$ Blakemore [6] have done tests on samples containing 0.08 at % hydrogen at temperatures ranging from -144 to -30°C at a strain rate of $1.37 \times 10^{-4} \text{ Sec}^{-1}$ At the extremes of temperature within this range the stress strain curves are smooth The serrated yielding is explained by considering obstruction in the motion of dislocations by diffusing hydrogen atoms resulting in locking and unlocking sequences [3] Above UCT, the interaction of hydrogen with dislocation becomes small and high hydrogen mobility enables it to keep up with the dislocation movement Serrated yielding thus disappears above this temperature On the other hand, below LCT the diffusion rate of hydrogen is insufficient to keep up with the rate at which dislocations are moving under the applied strain rate, and so no locking and unlocking occurs The appearance of serrated yielding and thus LCT and UCT depends upon strain rate [3,4] Above and below certain strain rates there will be no serrated yielding The influence of hydrogen content has also been reported [6]

Table 1 represents the values for the activation energy for hydrogen diffusion in nickel

TABLE 1 [31]

		UCT (ev)	LCT (ev)	Differ- ence (UCT-LCT) (ev)	From Condensation (ev)
Boniszewski and Smith	[3]	0.36	0.33	0.03	0.12
Windle and Smith	[8]	1.74	0.27	1.44	0.14
Blakemore	[6]	0.71	0.59	0.12	0.14
Combette and Grilhe	[7]	0.41	0.26	0.15	0.15

The activation energy in the last column has been calculated by using Cottrell's [21] condensation equation and assuming UCT to be the temperature at which condensation of the hydrogen occurs in the dislocations. The spread in the values tabulated may be due to experimental errors, purity of nickel and hydrogen concentration inspite of the fact that there is no significant change in the results because of different hydrogen levels [6]. The difference between the values of activation energies at UCT and LCT has been said to be bounding energy of the diffusing atom to a dislocation. Except Blakemore, no one has tried to explain as to how these energies arise? He has considered elastic misfit, Suzuki locking and

electrical interaction. The first two were discarded because there was negligible change in lattice parameter of nickel by hydrogen charging. He stated the likelihood of formation of local region of hydride in the dislocations because of an electrical interaction between the dislocations and the hydrogen atoms dissolved as protons.

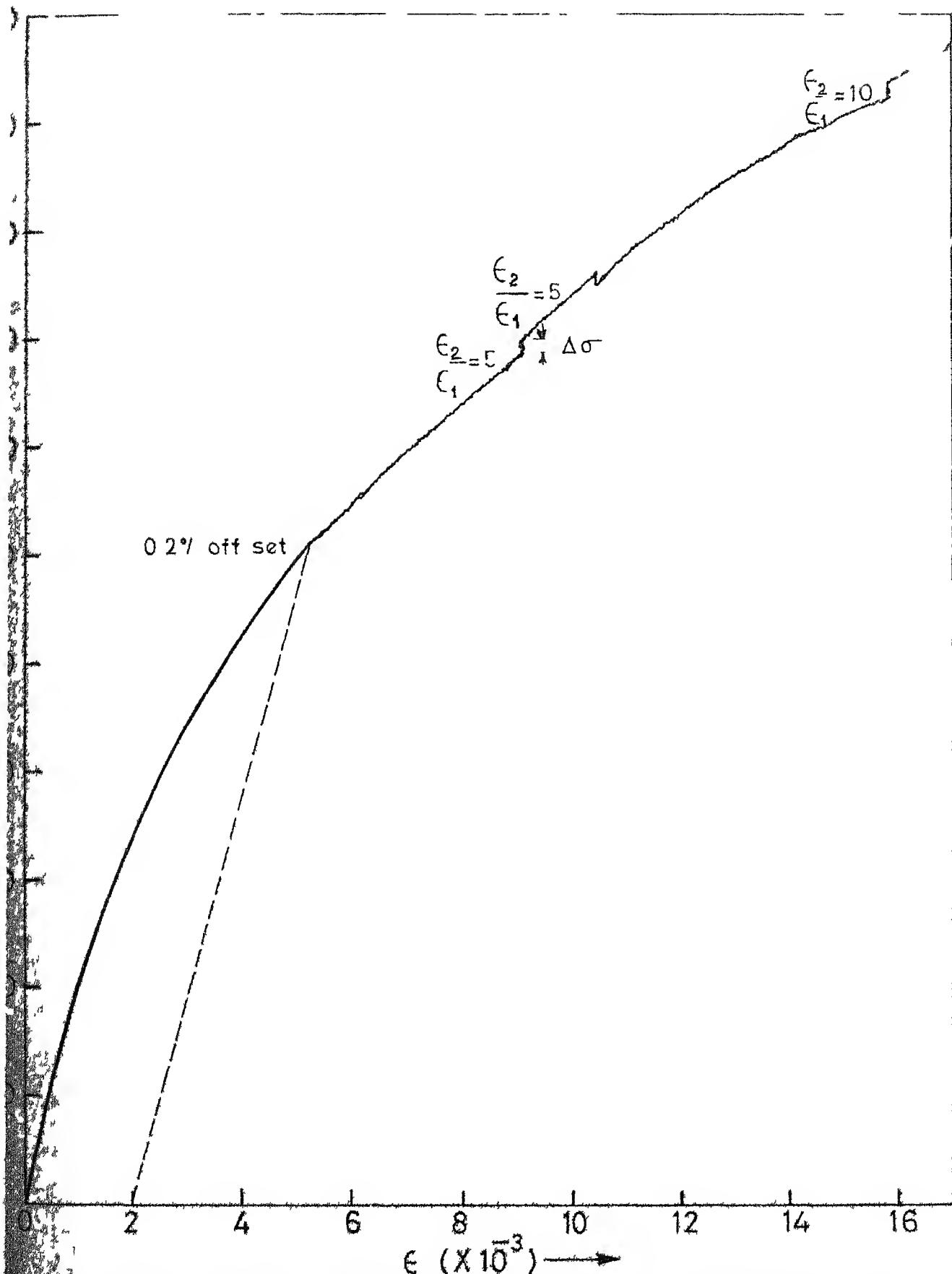
The last feature of serrated yielding is the overall increase in the rate of work-hardening, in comparison with hydrogen free nickel, because of dislocation multiplication resulting in a greater dislocation density at a given strain and hence higher flow stress [4].

CHAPTER 3EXPERIMENTATION

Samples for tensile test were prepared from 99.99% purity nickel rods of 1/8" diameter supplied by Semi Elements Inc., U.S.A. The rods were cut into suitable gauge lengths, vacuum annealed at 800°C for one hour and then straightened by plastically deforming to a strain of about 0.1%. The straight samples were re-annealed in vacuum to remove internal stresses and then charged with purified hydrogen at 800°C for one hour and furnace cooled to room temperature under hydrogen atmosphere. After this treatment the samples generally had a grain size of about 100 microns.

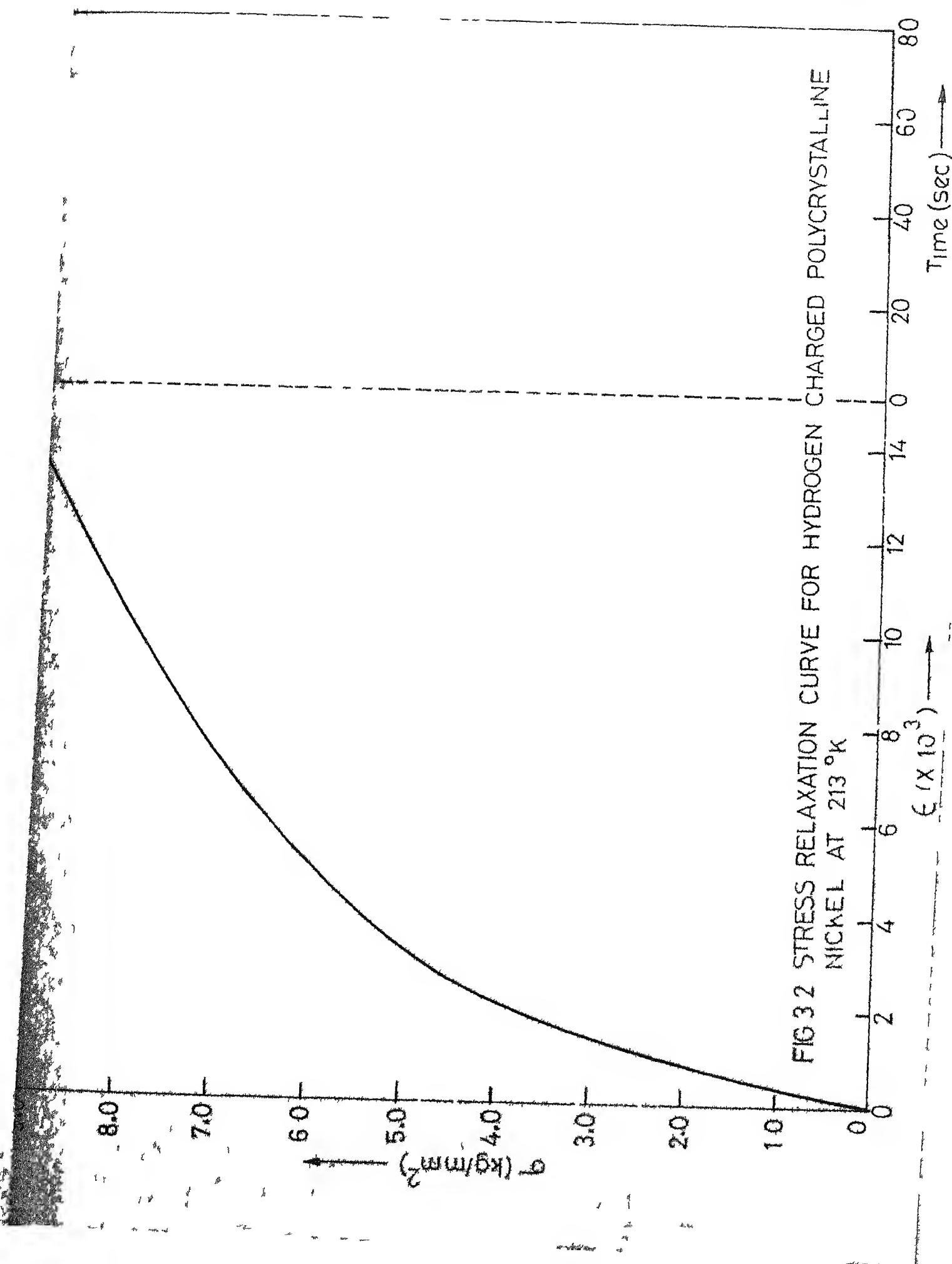
Hydrogen charged samples were tested in floor model INSTRON machine at various temperatures, from room temperature to liquid nitrogen temperature. The temperatures chosen were room temperature (293°K), 273°K, 213°K, 173°K and 77°K by using suitable temperature baths.

Activation energies were determined from incremental stresses obtained from instantaneous strain rate change experiments made close to yield point by changing the strain rate from a basic value $\dot{\epsilon}_1$ to



STRESS STRAIN CURVE FOR HYDROGEN CHARGED POLYCRYSTALLINE NICKEL AT 213°K SHOWING CHANGE IN σ ($\Delta \sigma$) WITH CHANGE IN STRAIN RATE ($\epsilon_2/\epsilon_1 = 5, 10$)

FIG. 3.2 STRESS RELAXATION CURVE FOR HYDROGEN CHARGED POLYCRYSTALLINE NICKEL AT 213 °K



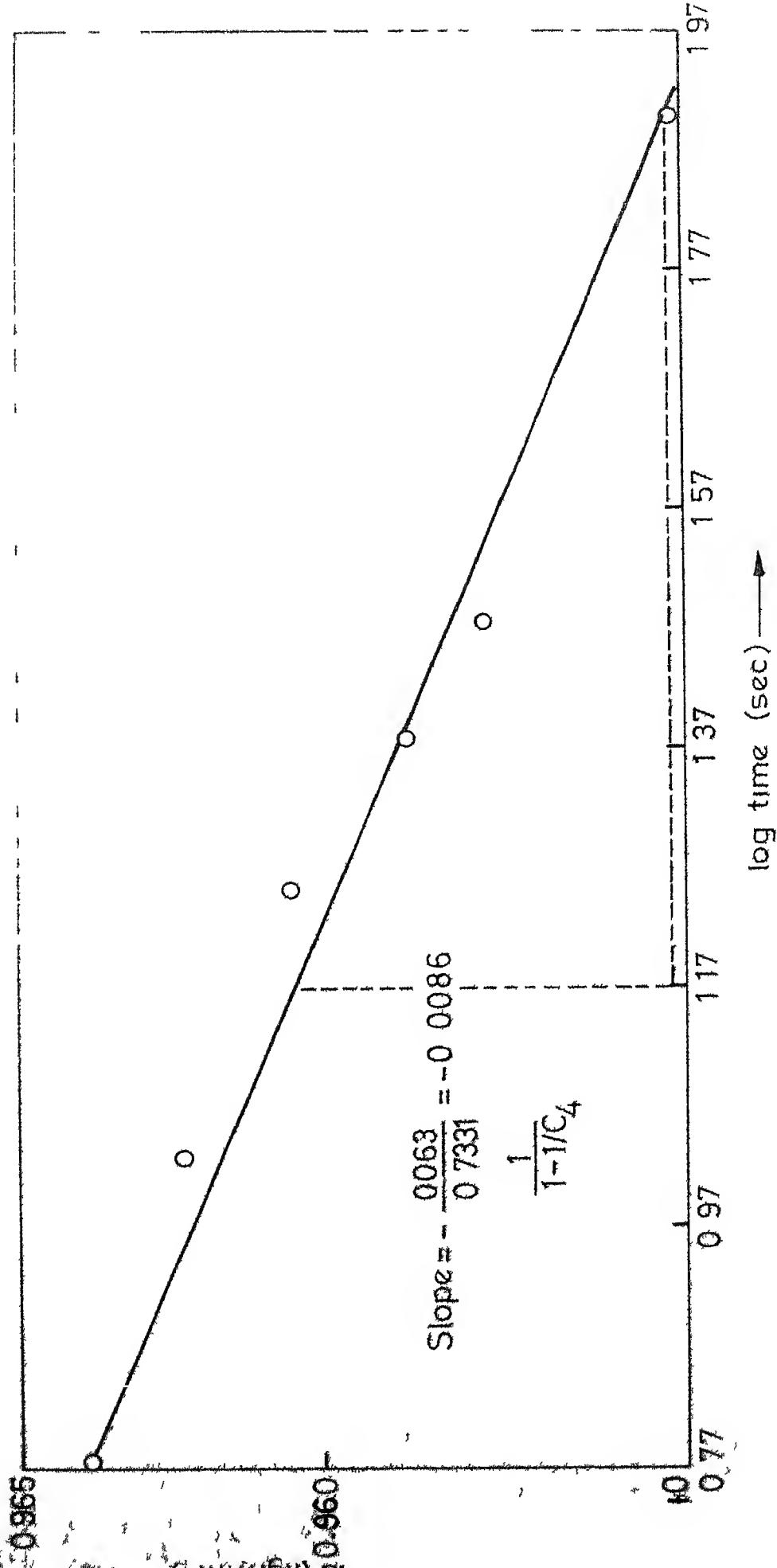


FIG 3.3 LOG PLOT OF STRESS RELAXATION CURVE FOR HYDROGEN CHARGED POLYCRYSTALLINE NICKEL AT 213°K

ϵ_2 ($\frac{\epsilon_2}{\epsilon_1} = 5$ to 10) Fig 3 1 is the representation of strain rate change experiment done at 213^0K The activation energies were obtained by using equations (4 3), (4 5) and (4 6) These values were in good agreement with the relaxation tests [32], figs 3 2 and 3 3 being the representation of relaxation test at 213^0K Here the slope of log stress (kg/mm^2) vs log time (sec) being $\frac{1}{1-1/C4}$ and using equations (4 3), (4 5) and (4 6), the activation energy values were obtained

CHAPTER 4RESULTS AND DISCUSSION

For plain Fe-C alloys, Yokobori [33] has given the thermal component of activation energy for release of a sufficient number of dislocations, U , from their locking carbon atmosphere as

$$U = - \frac{1}{n} \ln \frac{\sigma}{\sigma_0} \quad (4 1)$$

Considering the theory of yielding proposed by Eontrell and Bilby [34] and equation (4 1), Campbell [35] obtained the following relationship for the yield strength in a constant strain rate test as

$$\sigma_y = \sigma_0 \left(\frac{C_3}{C_4} \epsilon \right)^{C_4} \quad (4 2)$$

here $C_4 = \frac{nkT}{1 + nkT} \quad (4 3)$

Taking logarithm of both sides of equation (4 2) and differentiating with respect to ϵ at constant temperature, T , we get

$$C_4 = \left(\frac{\partial \log \sigma_y}{\partial \log \epsilon} \right)_T \quad (4 4)$$

or $C_4 = \frac{\epsilon \sigma / \sigma_0}{2.303 \log(\epsilon_2 / \epsilon_1)} \quad (4 5)$

C_4 is determined by performing strain rate change tests close to yield at different temperatures and the material constant, n , is then obtained from equation

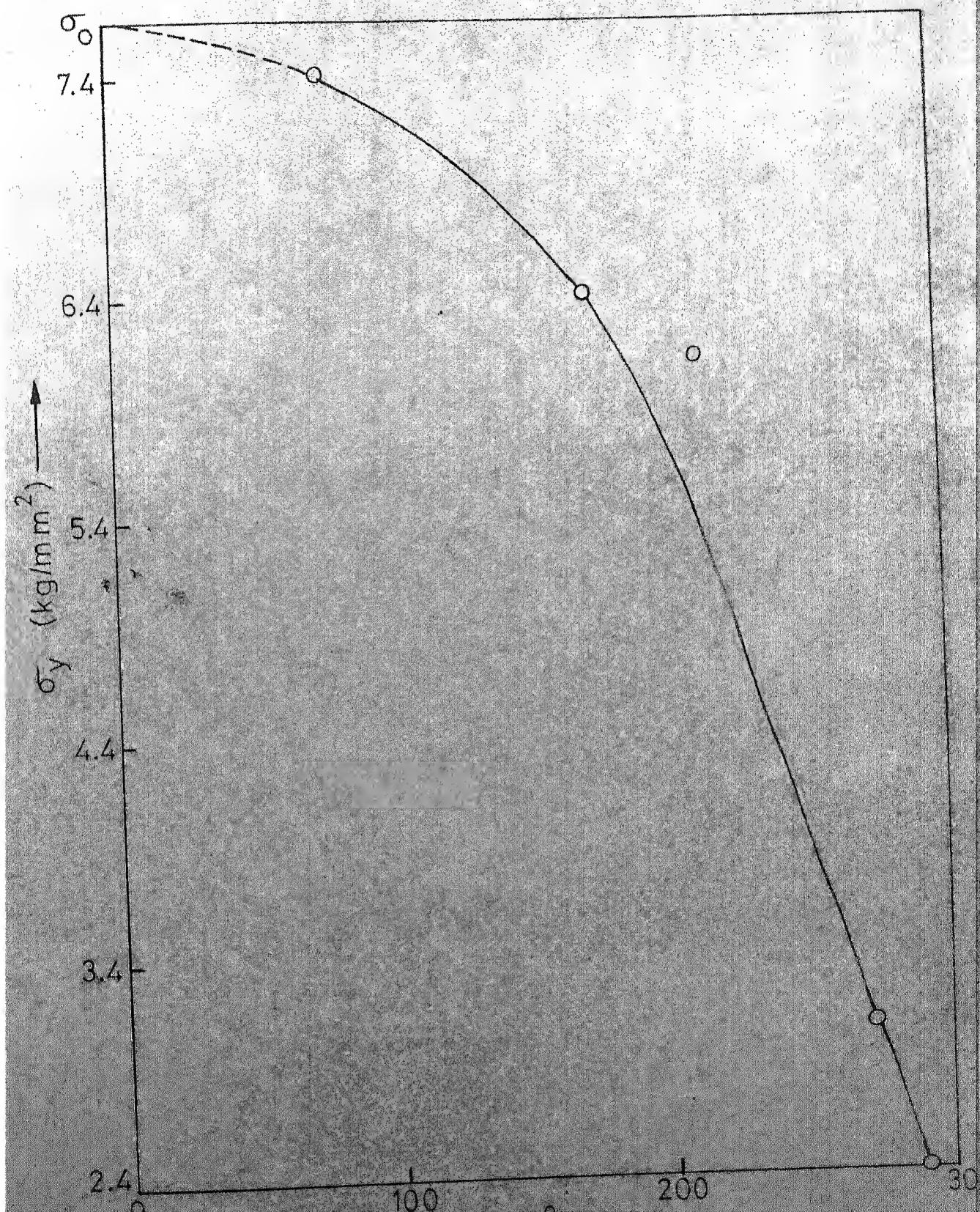
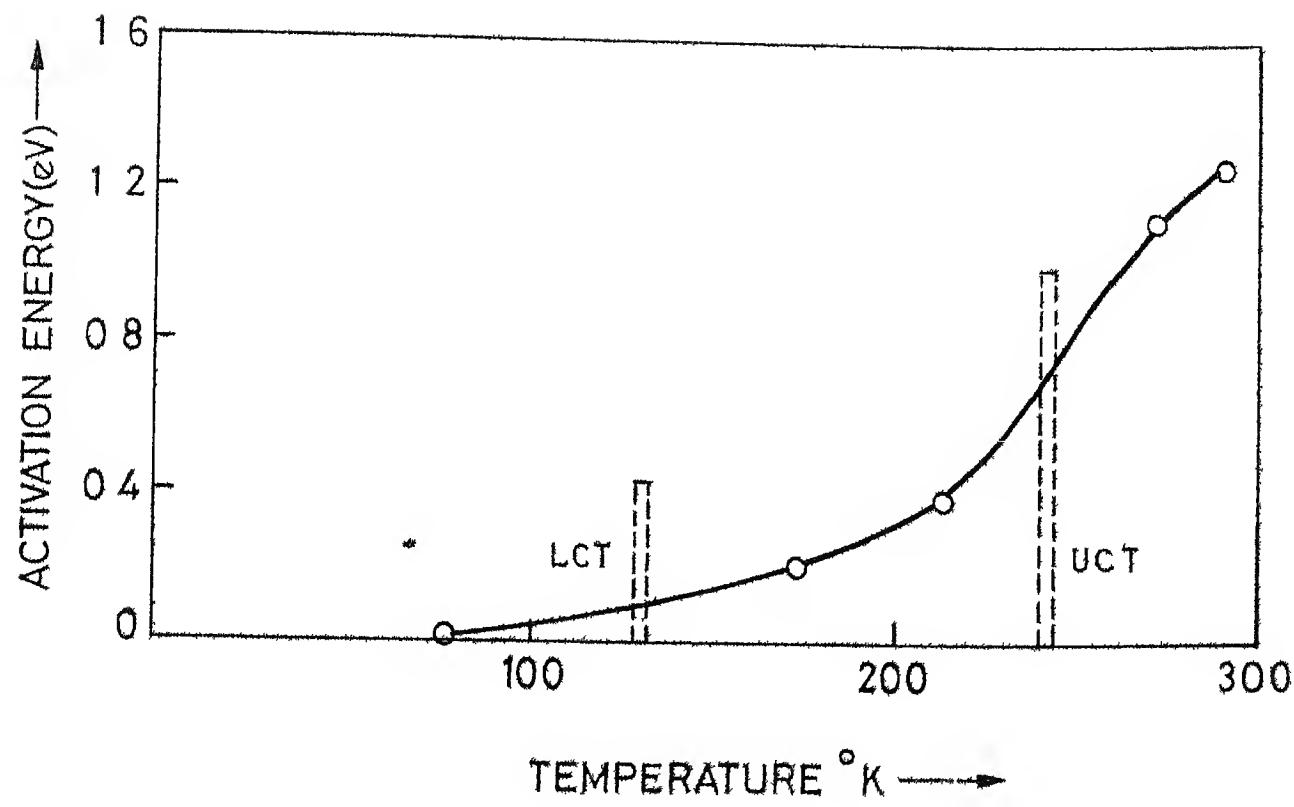


FIG. 4.1 VARIATION OF EXPERIMENTALLY MEASURED YIELD STRESS (σ_y) OF HYDROGEN CHARGED POLYCRYSTALLINE NICKEL AS A FUNCTION OF TEMP. (T)



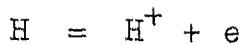
(4 3) σ_0 and n are also determined independently from relaxation tests [32] and found to be in good agreement with those determined by strain rate change experiments

The value of σ_0 is obtained by extrapolating the 0.2% off-set yield stress versus temperature curve (Fig. 4 1) A correction for the temperature dependence of the shear modulus, G , was applied in equation (4 1) from a reconstructed curve of G vs T by using the $(\frac{dG}{dT})$ values of Haasen [36] Thus equation (4 1) can be rewritten as

$$U = -\frac{1}{n} \ln \frac{\sigma/G}{\sigma_0/G_0} \quad (4 6)$$

The activation energy, U , is then determined from equation (4 6), and is shown in figure 4 2 as a function of temperature UCT and LCT, shown in figure 4 2, correspond to the onset of serrations and the disappearance of serrations respectively The activation energy determined this way is found to be in general agreement with those determined by other investigators (Table 1) but is found to be strongly temperature dependent between LCT and UCT

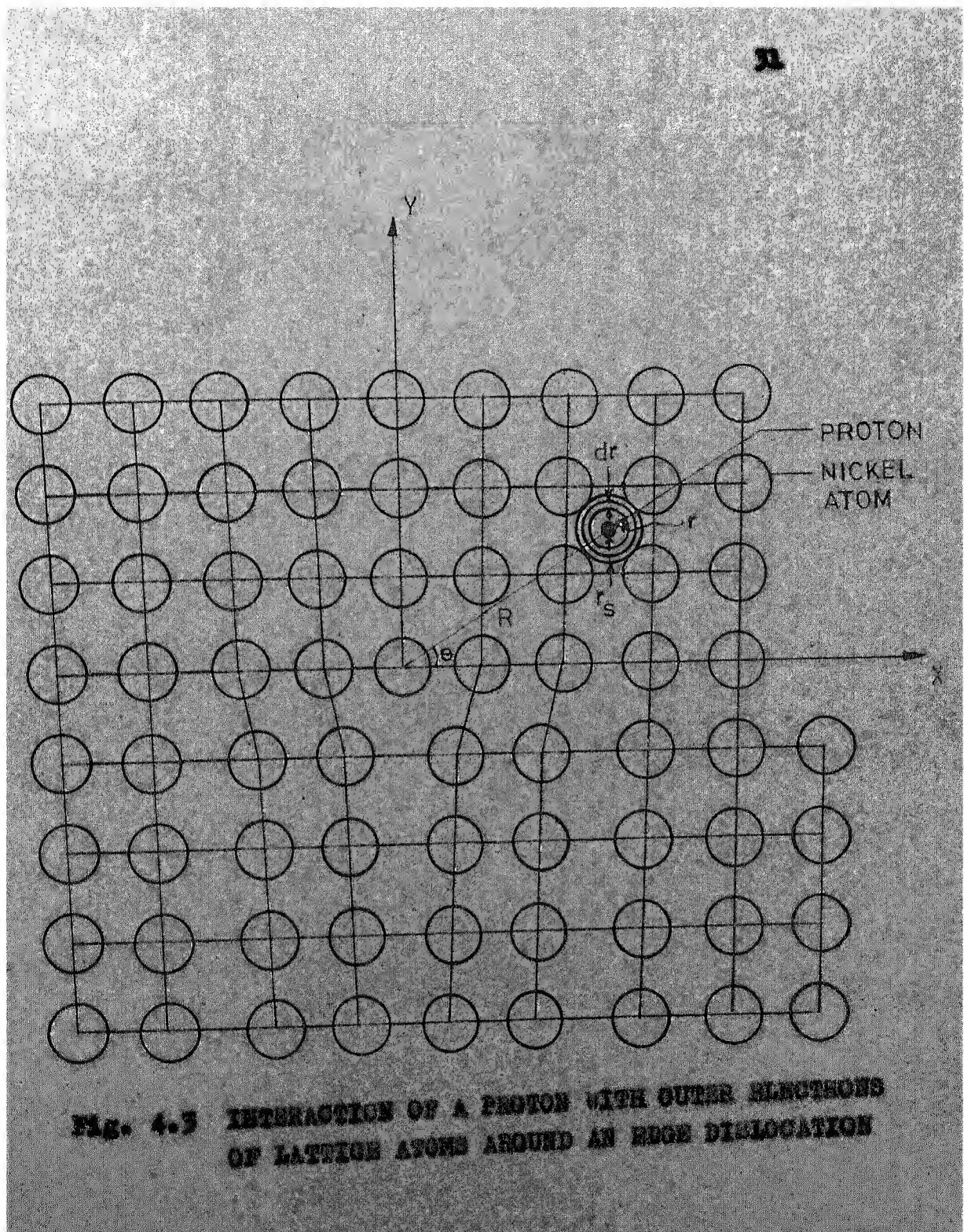
The temperature dependence of activation energy is explained by considering hydrogen dissociation into an electron and a proton with the electrons entering the unfilled bands of nickel [37]



It is suggested that the dissociation of hydrogen atom into a proton and an electron is partial at low temperatures and is complete at higher temperatures. Thus at very low temperatures we have purely elastic or electrostatic type of interaction between hydrogen atom and dislocations but as the temperature is increased, the dissociation of hydrogen atom takes place and we have both elastic interaction between hydrogen atoms and dislocations and interaction between protons and dislocations. At room temperature hydrogen is supposed to be completely dissociated with a small activation energy of about 0.1 eV for dissociation [38] and around these temperatures the interaction may be expected to be completely between protons and dislocations.

The associated interaction energy may be estimated by the jellium approximation given by Kittel [39] by calculating the total electrostatic energy of interaction, U_c , of a proton within a sphere of radius r_s containing a uniformly distributed charge $-e$. To perform this analysis we can write for the net charge around a proton within a sphere of radius $r < r_s$ (Fig. 43) and lying in a dislocated region as

$$q(r) = e[1 - \alpha^* (r/r_s)^3] \quad (47)$$



where $\alpha^* = \alpha (1 + \Delta)$ (4.8)

and $\Delta = \frac{b}{2\pi} \frac{1-2V}{1-V} \frac{\sin\theta}{R}$ for an edge

dislocation. Thus, the electrostatic potential at a radius r is $\phi(r) = q(r)/r$, and the electrostatic potential energy of a shell of thickness dr at r is

$$dU_c = (4\pi r^2 \rho dr) e [1 - \alpha^* (r/r_s)^3] / r \quad (4.9)$$

where ρ is given by

$$\rho = -\alpha^* e / \left(\frac{4}{3}\pi r_s^3\right) \quad (4.10)$$

Integrating equation (4.9) we obtain the coulomb energy per atom, U_c , to be

$$U_c = -\frac{3\alpha^*}{10} \frac{e^2}{r_s} (5 - 2\alpha^*) \quad (4.11)$$

The total energy per atom is $U_0(r_s) = U_c + U_F$, where U_F is the average kinetic energy of the Fermi gas, given by [40]

$$U_F = \frac{3}{5} \frac{k^2}{2m} k_{\max}^2 \quad (4.12)$$

where k_{\max} can be represented by [41]

$$\frac{1}{2} N = \frac{1}{8} \frac{4\pi}{3} k_{\max}^3 \quad (4.13)$$

$$\text{and } N = \frac{3\alpha^*}{4\pi r_s^3} \quad (4.14)$$

Using equations (4.12), (4.13) and (4.14), the expression

for U_F can be written as

$$U_F = \frac{3}{10} \left(\frac{9\alpha^* \pi}{4} \right)^{2/3} \frac{e^2}{m} \frac{1}{r_s^2} \quad (4.15)$$

The equilibrium value of r_s may be obtained by minimizing

$$U_0(r_s) = U_C + U_F = - \frac{3\alpha^*}{10} \frac{e^2}{r_s} (5-2\alpha^*) + \frac{3}{10} \left(\frac{9\pi\alpha}{4} \right)^{2/3} \frac{e^2}{m} \frac{1}{r_s^2} \quad (4.16)$$

to be

$$r_s = \frac{3 \cdot 9}{\alpha^{*1/3} (5-2\alpha^*)} A^0 \quad (4.17)$$

The corresponding energy is obtained by substituting equation (4.17) in equation (4.16) to be

$$U_0 = -0.555 (5-2\alpha^*)^2 \alpha^{*4/3} \text{ eV} \quad (4.18)$$

From equations (4.8) and (4.18) we get,

$$U_0 = -0.555 [\alpha(1+\Delta)]^{4/3} [(5-2\alpha)^2 - 4\alpha \Delta (5-2\alpha) + 4\alpha^2 \Delta^2]$$

For $\Delta \ll 1$,

$$\begin{aligned} U_0 &= -0.555 \alpha^{4/3} (5-2\alpha)^2 + 0.555 \alpha^{4/3} [4\alpha \Delta (5-2\alpha) - \frac{4}{3} \Delta (5-2\alpha)^2 - 4\alpha^2 \Delta^2 \\ &\quad + \frac{16}{3} \alpha \Delta^2 (5-2\alpha) - \frac{16}{3} \alpha^2 \Delta^3] \\ &= A + U_1 \end{aligned} \quad (4.19)$$

where $A = -0.555 \alpha^{4/3} (5-2\alpha)^2$ and

$$U_1 = 0.555 \alpha^{4/3} [4\alpha \Delta (5-2\alpha) - \frac{4}{3} \Delta (5-2\alpha)^2 - 4\alpha^2 \Delta^2 + \frac{16}{3} \alpha \Delta^2 (5-2\alpha) - \frac{16}{3} \alpha^2 \Delta^3]$$

The first term $0.555\alpha^{4/3}[4\alpha\Delta(5-2\alpha)]$ in U_1 is somewhat analogous to the electrostatic interaction energy term obtained by Cottrell, Hunter and Nabarro [42]. Here the sign for Δ is chosen in such a way that the total proton - dislocation interaction energy becomes more negative giving rise to an attractive interaction energy. The variation of U_1 as a function of dialatation Δ , and electron density α is shown in figure 4.4. The different types of interaction energies, including elastic interaction and electrostatic interaction etc are also shown in the same figure. A good agreement between experimentally measured values of activation energy and the calculated proton-dislocation binding energy is obtained for values of the dialatation, Δ , between -0.1 and -0.15 which is commonly used for elastic interaction calculations and by choosing $1 < \alpha < 1.6$.

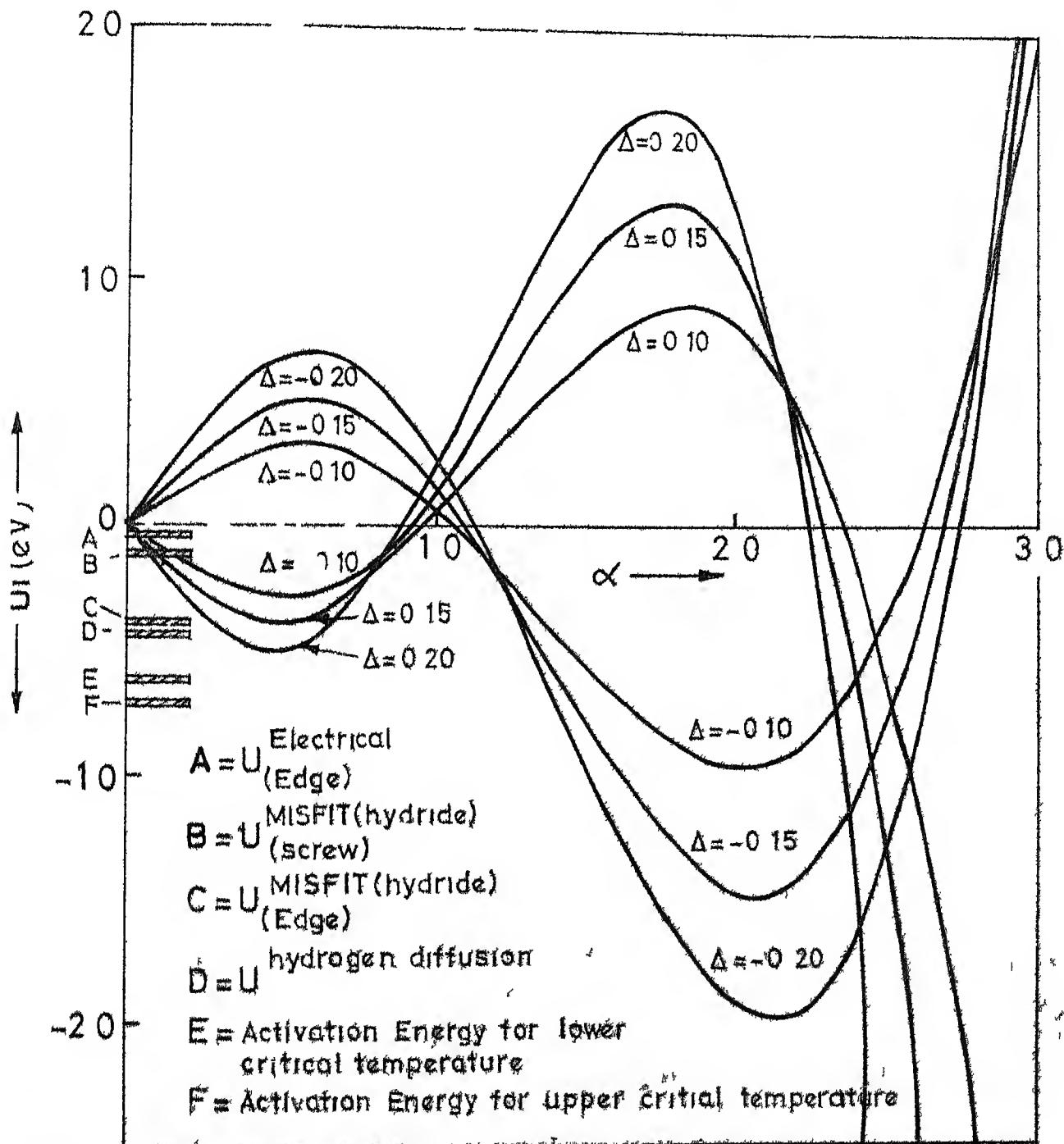


Fig. 4.4 Activation energies for the formation of a hydride phase at 2000 K as a function of the hydride concentration α for different values of Δ .

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